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Description of EP0878319

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The invention relates to a recording sheet for the ink jet compression matter (Inc. jet method).

The Inc. jet method belongs to the electronic compression matters. Here it is possible, pictures, to build and print out as screen hardcopy texts and graphics up at the computer directly.

With the Inc. jet method droplets of a recording liquid are laid on on the surface of the carrier material by means of different techniques. For drop production there are in principle two procedure variants.

With the method of the continuous drop production under letterpress printing a permanent droplet stream from the nozzle is driven. The drops unnecessary for the screen layout are supplied to the ink storage vessel by different principles again.

With the drop on and method is produced only in the setting to call an ink droplet, which can be illustrated. By a digital electronic control, like with the cycles per second method, is possible it to produce pictures with very high resolution directly from electronic data.

The Inc. jet recording method is used full color copies to the preparation by color graphics, and also for text pressures, it enclosure thus a very broad application field.

Against the recording sheet different demands are made like print gloss, color running (Bleed), color density, drying behavior, unrest (Mottle), poor copy and gloss.

The receipt material consists generally of a carrier material, an ink receipt layer and if necessary further auxiliary layers.

The DE 37 07 627 describes an ink photograph layer, which consists of two polymer units with a quaternary ammonium compound and a pigment. Thus one achieves a high color density, a good ink absorption and a good water resistance. However the gloss is so strongly reduced by the high pigment portion that it can be increased also by a Kalandrierung not substantially. Under the used paper, is to be counted also on the dropping of the ink photograph layer.

The JP 01-009776 and the JP 01-075281 describe an ink photograph layer with good contrast, good light and water resistance, which of a copolymer and an adhesive/pigment mixture consist. The copolymer sits down together from a Dimethyldiallylammoniumchlorid and an acrylamide. It comes also here by the pigment portion to a gloss loss.

The DE 43 22 178 suggests a pigmenthaltige ink photograph layer, which likewise contains a quaternary ammonium compound for the reaching of high color density and image focus.

As is the case for the writings stated above also here the retention of the dyes from the ink is reached by the addition of the pigment and is connected with a gloss reduction.

The EP 0,627,324 describes a recording sheet for the ink jet compression matter, with which in the receipt layer a Terpolymer of a quaternary ammonium compound is used. Additionally an epoxy or a Triazin is admitted as crosslinking agent. Thus running out the color points and a heterogeneity of the color and the density are prevented. Unfavorable however an extension of the drying time and a worse color admission. By a polymerizing of the quaternary ammonium compound into the Terpolymer the control possibility for the optimization of the Farbstoffierung decreases.

The DE 43 22 178 describes a recording sheet for the Inc. jet compression matter a glued Rohpapier as carrier material. To it an occurrence of gloss differences with that is unfavorable printed material.

Task of the invention is it to make a recording sheet available for the Inc. jet compression matter by high color density, high gloss, good drying characteristics, high color brilliance and small color running with low pick-up of the receipt layer is characterised.

This task is solved by a recording sheet, which contains a carrier and an ink photograph layer arranged on it which contain a unvernetztes copolymer, consisting of a quaternary ammonium compound and vinyl pyrrolidone, a polyvinyl alcohol and a Aminomethacrylat copolymer.

For the better Farbstoffierung and improvement of the drying characteristics a hydroxyfunktionelles, quaternary, amino groups containing polymer are inserted on base of alkyl (meth) acrylic acid ester or alkyl (meth) acrylamide and a polyvinyl alcohol than further adhesive.

Part-soaped and full-soaped polyvinyl alcohols are suitable.

Further components of the ink photograph layer can be polyvinylpyrrolidone (PVP) - Homopolymere, farbstoffierende compositions, optical Autheller, dyes and other auxiliary materials.

Since the carrier material can differ in the gloss values depending upon preparation, it is necessary in some felling, pigments of the ink photograph layer to add, which make an adjustment possible of the gloss. To the control of the gloss pigments can be added such as calcium carbonate, titanium dioxide, Clay, silicon dioxide, Bentonit, aluminium oxide or boehmite. The quantity of the pigments in the ink photograph layer can do 0 and 5 Gew.%, related to which dried

coating amount to.

The weight-related portion of the copolymer of the ink photograph layer can amount to 5 to 80% Gew.% and in a more preferential form 15 to 50 Gew.%.

The portion of the hydroxylfunktionellen, amino groups of containing polymer preferably is with 5 to 75 Gew.% and in a still more preferred embodiment with 15 to 50 Gew.%. The portion of the polyvinyl alcohol can do 5 to 80 Gew.% and in accordance with a still more preferred embodiment with 30 to 60 Gew.%.

The pick-up of the dried receipt layer can do 2 to 15g/m<sup>2</sup> and preferably 4 to 10g/m<sup>2</sup> amounted to.

The aqueous coating mass can vary in the following weight quantities:

```
< tb> < TABLE> Columns= 2
< tb>
< tb> Head Col 1:
< tb> Head Col 2: Thread. %
< tb> Vinylpyrrolidon/Methacrylamidopropyltrimethylammoniumchlorid Copolymer< SEP> 2,2 - 60,0
< tb> Aminomethacrylat< SEP> 2,2 - 57,0
< tb> Polyvinylalkohol< SEP> 3,0 - 80,0
< tb> Hilfestoffe< SEP> 0,0 - 20,0
< tb> Wasser< SEP> Remainder to 100,0
< tb> < /TABLE>
```

The Beschichtungsmasse to the preparation of the ink photograph layer according to invention can with all common order and dosing procedures, as walzenauftrag, engraving or siphon methods and Luftbürsten or roll blade dosage are laid on.

In a special arrangement between the carrier material and the receipt layer additionally an intermediate layer is laid on. The intermediate layer preferably contains polyvinyl alcohol; in addition, connections are suitable such as polyvinylpyrrolidone or polyvinyl acetate or their mixtures. For this intermediate layer one obtains a high print gloss, since dropping the receipt layer is prevented with papers without synthetic resin coating.

Since the surface of paper always exhibits a certain porosity, parts of the coatings are taken up by the paper.

The print gloss will at the printed paper, particularly with dark surfaces visibly and should over the entire surface be uniform. High print gloss expresses itself in a smooth shining coating. With papers, which are coated with synthetic resin, by this intermediate layer the adhesion of the receipt layer at the carrier material is improved, postponing the receipt layer in the presser is prevented in such a way.

The pick-up of the dried intermediate layer can do 0.1 to 4,0g/m<sup>2</sup> , preferably 0.5 to 2,0g/m<sup>2</sup> > amounted to.

As carrier materials prefer papers, those are suitable are reciprocally with synthetic resin coated and so-called castingcoated (castcoated) papers. As particularly important thereby a very smooth, even surface proved. The surface roughness (RA) according to DIN 4768 may not exceed a value of 0,8 µm with a measuring section of 5mm.

The papers reciprocally coated with synthetic resin g/m<sup>2</sup> a weight per unit area from 50 to 250; 2>. As synthetic resin for example polyolefins or polyesters are used.

The order quantity of the synthetic resin coating amounts to at least 5 g/m<sup>2</sup> >. Can be contained in this coating additionally still pigments, dyes and other auxiliary materials.

Further castingcoated paper proved as particularly suitably. These papers will provide containing surface line in the paper machine with a thin adhesive and pigment and under pressure against a hot high polish drum printed. Thus one receives papers with a good, shining surface, which the disadvantages of hochkalanderten papers do not show. Opposite synthetic resin-coated papers this has the advantage of very low drying times. The weight per unit area lies with this paper between 50 g/m<sup>2</sup> > and 270 g/m<sup>2</sup> >. The gloss of the paper with intermediate layer, measured with 60° 0> , than 80%, there the gloss of the basis paper, under the small pick-up of the ink photograph layer, may not be smaller strongly on the finished recording sheet affects itself. The print gloss must amount to with papers without intermediate layer at least 65%, with intermediate layer at least 75%.

In addition, as carrier material an uncoated or painted basis paper is suitable.

The following examples are to describe the invention more near.

Examples:

The front of a polyethylene-coated basis paper was coated with the coating masses B1 to B6.

```
< tb> < TABLE> Id= Tabelle 1 Columns= 7
< tb>
< tb> Head Col 1: Composition
< tb> Head Col 2: B1
< tb> Head Col 3: B2
< tb> Head Col 4: B3
< tb> Head Col 5: B4
< tb> Head Col 6: B5
< tb> Head Col 7: B6
< tb> Polyvinyl alcohol 15%
1)
< SEP> 26,23< SEP> 30,77< SEP> 22,86< SEP> 57,14< SEP> 38,4< SEP> 28,2
< tb> VP MAPTAC copolymer 20%
2)
< SEP> 14,76< SEP> 11,54< SEP> 17,15< SEP> 7,14< SEP> 11,5< SEP> 10,1
< tb> Aminomethacrylat copolymer 20%
3)
< SEP> 14,75< SEP> 23,08< SEP> 8,57< SEP> 21,42< SEP> 11,1< SEP> 9,7
```

< tb> Alumina hydroxide hydrate 15%

4)

< SEP> < SEP> < SEP> < SEP> 3,9< SEP> 16,2

< tb> Wasser< SEP> 44,26< SEP> 34,61< SEP> 51,42< SEP> 14,3< SEP> 35,1< SEP> 35,8

< tb> Order g/m< 2> < SEP> 6,9< SEP> 10,8< SEP> 5,2< SEP> 8,5< SEP> 7,6< SEP> 7,8

< tb> Solid %< SEP> 9,8< SEP> 11,5< SEP> 8,6< SEP> 14,3< SEP> 10,9< SEP> 10,6

all data in Gew. %

1) Mowiol TM 10-74

2) Vinylpyrrolidon/Methacrylamidopropyltrimethylammoniumchlorid copolymer, Gafquat TM HS-100,

3) Induquat TM ECR 766/964 I,

4) Martoxin TM VPP 9507

< tb> < /TABLE>

As underlay a reciprocally polyolefin-coated basis paper with a total area weight of 160 served g/m< 2> and a RA value of 0,512, measured on the polyolefin-coated surface of the basis paper.

The back of the basis paper was coated with a LDPE (low density polyethylene). The pick-up amounted to 22 g/m< 2> . The front with a LDPE with a titanium dioxide content of 10 Gew.% coats the pick-up amounted to 19 g/m2.

Used for the examples B7 to B12 in place of the polyolefin-coated basis paper a commercial castcoated paper. The total weight amounted to 215 g/m< 2> . Commercial papers are the Cromoluxpapiere of the company Zanders or the Lustruluxpapiere of Tullis Russell.

For B7 the coating mass was used by example 1.

For B8 the coating mass was used by example 2.

For B9 the coating mass was used by example 3.

For B10 the coating mass was used by example 4.

For B11 the coating mass was used by example 5.

For B12 the coating mass was used by example 6.

As intermediate layer B7 to B9 became a high-molecular polyvinyl alcohol with the examples B1 to B3 and (Mowiol< TM > 96-98) with a pick-up of 0,8g/m< 2> laid on.

With the examples B4 to B6 and B10 to B12 became as intermediate layer polyvinylpyrrolidone (Luviskol< TM > K90) with a pick-up of 1,7g/m< 2> selected.

As example the underlay and the coating mass of example 7, an intermediate layer served 13 with this example were not laid on.

Comparison examples V1 to V3

< tb> < TABLE> Id= Tabelle 2 Columns=4

< tb>

< tb> Head Col 1:

< tb> Head Col 2: V1

< tb> Head Col 3: V2

< tb> Head Col 4: V3

< tb> Aminomethacrylat copolymer 10%

1)

< SEP> 51,22< SEP> 75,9< SEP> 44,94

< tb> Polyvinyl alcohol 7%

2)

< SEP> 48,78< SEP> 12,05< SEP> 27,53

< tb> Polyvinylpyrrolidone 7%

3)

< SEP> < SEP> 12,05< SEP> 27,53

< tb> Order g/m< 2> SEP> 15,8< SEP> 15,4< SEP> 12,8

< tb> Solid %< SEP> 13,6< SEP> 16,6< SEP> 12,5

1) Induquat TM ECR 766/964 I

2) Gohsenol GM 14

3) Luviskol TM K 90

< tb> < /TABLE>

As underlay the polyolefin-coated paper of the examples served B1 to B6.

As comparison example the example 1a from the DE 43 22 178 served V4.

Testing of the Aufzeichnungs materials received in accordance with example B1 to B13 and comparison example V1 to V3.

On the recording sheet with a commercial Inc. jet color printer by HEWLETT PACKARD, new fact jet, and the appropriate inks a test pattern was imprinted. This test pattern was examined on color density, running, Mottle, Farblüxierung and poor copy. The results of these testings are summarized in the tables 3 and 4.

## 1. Color density:

The Farbdesitität was based with a X-guessing Desitometer type 428 on the colors cyanogen, Magenta, yellow and black.

## 2. Run (Bleed):

The Ineinanderverlaufen of the inks at the edges of lying together color surfaces was judged visually with the notes 1 to 6 (very well to very badly).

## 3. Unrest (Mottle):

Unrest or also Wolkigkeit in a color surface was visually judged with the notes 1 to 6 (very well to very badly).

## 4. Farbfixierung:

To the testing of the Farbfixierung the print format was abraded after 24 hours of storage with 23 DEG C with a white lapping. The transmission of the ink was evaluated on the lapping for the colors cyanogen, Magenta and yellow. The transmission of black was separately evaluated (+ no transmission, - transmission).

## 5. Poor copy:

To the testing poor copy the print format was covered after 5 minutes and after 15 minutes with a PTS basis paper and loaded with a 10 kg weight 24 hours. Subsequently, that was judged visually poor copy of the ink by the ink receipt layer on the PTS paper with the notes 1 to 6 (no poor copy to very strong poor copy).

## 6. Gloss

The gloss became with a gloss measuring instrument the Dr. Long GmbH according to DIN 67530, with an angle of 60< 0> measured. The measuring was accomplished at the blank receipt material.

## 7. Print gloss

The print gloss became likewise with a gloss measuring instrument the Dr. Long GmbH according to DIN 67530, with an angle of 60< 0> measured. The measuring was accomplished on a black printed part of the receipt material.

Results of the color density measurements of the gloss measurement and the print gloss measurement of the examples B1 to B13 and the comparison examples V1 to V

```
< tb> < TABLE> Id=Tabelle 3 Columns=7
< tb>
< tb> Head Col 1:
< tb> Head Col 2: Cyanogen
< tb> Head Col 3: Magenta
< tb> Head Col 4: Yellow
< tb> Head Col 5: Black
< tb> Head Col 6: Gloss
< tb> Head Col 7: Print gloss
< tb> < SEP> B1< SEP> 2,18< SEP> 1,51< SEP> 2,03< SEP> 2,29< SEP> 92,5< SEP> 88,7
< tb> < SEP> B2< SEP> 2,16< SEP> 1,53< SEP> 1,95< SEP> 2,15< SEP> 90,9< SEP> 87,2
< tb> < SEP> B3< SEP> 2,18< SEP> 1,45< SEP> 2,04< SEP> 2,33< SEP> 93,1< SEP> 89,1
< tb> < SEP> B4< SEP> 2,05< SEP> 1,41< SEP> 1,94< SEP> 2,52< SEP> 92,7< SEP> 88,7
< tb> < SEP> B5< SEP> 2,16< SEP> 1,55< SEP> 1,95< SEP> 2,14< SEP> 91,1< SEP> 87,3
< tb> < SEP> B6< SEP> 2,14< SEP> 1,55< SEP> 1,99< SEP> 2,17< SEP> 89,2< SEP> 86,6
< tb> < SEP> B7< SEP> 2,16< SEP> 1,52< SEP> 2,01< SEP> 2,28< SEP> 88,5< SEP> 83,4
< tb> < SEP> B8< SEP> 2,18< SEP> 1,51< SEP> 1,96< SEP> 2,31< SEP> 87,3< SEP> 82,9
< tb> < SEP> B9< SEP> 2,15< SEP> 1,53< SEP> 1,98< SEP> 2,29< SEP> 88,1< SEP> 83,1
< tb> < SEP> B10< SEP> 2,17< SEP> 1,52< SEP> 2,01< SEP> 2,31< SEP> 88,5< SEP> 83,9
< tb> < SEP> B11< SEP> 2,19< SEP> 1,55< SEP> 1,95< SEP> 2,27< SEP> 88,6< SEP> 83,8
< tb> < SEP> B12< SEP> 2,17< SEP> 1,52< SEP> 1,88< SEP> 2,39< SEP> 87,4< SEP> 82,5
< tb> < SEP> B13< SEP> 2,14< SEP> 1,52< SEP> 1,99< SEP> 2,24< SEP> 87,2< SEP> 80,5
< tb> < SEP> V1< SEP> 2,14< SEP> 0,98< SEP> 1,99< SEP> 2,01< SEP> 87,5< SEP> 78,1
< tb> < SEP> V2< SEP> 2,05< SEP> 0,95< SEP> 1,99< SEP> 2,09< SEP> 87,7< SEP> 78,3
< tb> < SEP> V3< SEP> 2,07< SEP> 0,98< SEP> 1,95< SEP> 2,02< SEP> 88,6< SEP> 78,8
< tb> < SEP> V4< SEP> 2,04< SEP> 0,97< SEP> 1,96< SEP> 2,04< SEP> 82,1< SEP> 73,9
< tb> < /TABLE>
```

Results of the testing on Bleed, Mottle, Farbfixierung and poor copy of the examples B1 to B13 and the comparison examples V1 to V3

```
< tb> < TABLE> Id=Tabelle 4 Columns=7
< tb>
< tb> Head Col 1:
< tb> Head Col 2: Bleed note
< tb> Head Col 3: Mottle note
< tb> Head Col 4: Farbl. C, M, G
< tb> Head Col 5: Farbl. Black
< tb> Head Col 6: Abkl.5 min. Note
< tb> Head Col 7: Abkl.15 min. note
< tb> < SEP> B1< SEP> 3< SEP> 2< SEP> +< SEP> +< SEP> 2< SEP> 1
< tb> < SEP> B2< SEP> 3< SEP> 2< SEP> +< SEP> +< SEP> 2< SEP> 1
```

< tb> < SEP> B3< SEP> 3< SEP> 2< SEP> +< SEP> +< SEP> 2< SEP> 1  
 < tb> < SEP> B4< SEP> 3< SEP> 2< SEP> +< SEP> +< SEP> 2< SEP> 1  
 < tb> < SEP> B5< SEP> 2< SEP> 3< SEP> +< SEP> +< SEP> 3< SEP> 3  
 < tb> < SEP> B6< SEP> 2< SEP> 3< SEP> +< SEP> +< SEP> 3< SEP> 2  
 < tb> < SEP> B7< SEP> 2< SEP> 2< SEP> +< SEP> +< SEP> 1< SEP> 1  
 < tb> < SEP> B8< SEP> 2< SEP> 2< SEP> +< SEP> +< SEP> 1< SEP> 1  
 < tb> < SEP> B9< SEP> 2< SEP> 2< SEP> +< SEP> +< SEP> 1< SEP> 1  
 < tb> < SEP> B10< SEP> 2< SEP> 2< SEP> +< SEP> +< SEP> 1< SEP> 1  
 < tb> < SEP> B11< SEP> 2< SEP> 2< SEP> +< SEP> +< SEP> 1< SEP> 1  
 < tb> < SEP> B12< SEP> 2< SEP> 2< SEP> +< SEP> +< SEP> 1< SEP> 1  
 < tb> < SEP> B13< SEP> 2< SEP> 2< SEP> +< SEP> +< SEP> 1< SEP> 1  
 < tb> < SEP> V1< SEP> 4< SEP> 3< SEP> -< SEP> +< SEP> 4< SEP> 3  
 < tb> < SEP> V2< SEP> 4< SEP> 4< SEP> -< SEP> +< SEP> 5< SEP> 3  
 < tb> < SEP> V3< SEP> 4< SEP> 4< SEP> -< SEP> +< SEP> 5< SEP> 3  
 < tb> < SEP> VA< SEP> 3< SEP> 4< SEP> -< SEP> +< SEP> 3< SEP> 2  
 < tb> < /TABLE>

The examples show that the gloss and the print gloss could be particularly improved in relation to the comparison examples substantially. Also with the other properties the inspection results improvements show in relation to the comparison examples.